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CATALYTIC OXIDATION OF SULFUR DIOXIDE USING ISOTOPIC TRACERS

NEW YORK UNIVERSITY

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CATALYTIC OXIDATION OF SULFUR DIOXIDE USING ISOTOPIC TRACERS

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ABSTRACT

Since SO_2 is an important atmospheric pollutant the mechanism of the oxidation of SO_2 over a commercial vanadium pentoxide catalyst was studied using an all glass, essentially gradientless reactor at temperatures of 470-480°C and concentrations up to several percent of SO_2. It is expected that the results will have application both in improving the design and operation of equipment in which SO_2 is oxidized to SO_3 and in suggesting new catalyst formulations.

A theoretical development was derived for the use of isotopic tracers to study the kinetics and mechanism of complex catalytic reactions. Relationships developed on the basis of steady state conditions are combined with principles of thermodynamics and transition state theory. The methodology offers a unique tool for interpretation of experimental data.

Data were obtained using radioactive ^{35}S and the stable isotope ^{18}O as tracers. It was shown that the employment of two tracers simultaneously and the employment of more than one level of marking while still maintaining a fixed overall reaction velocity were often advantageous.

In the case of SO_2 oxidation, it was shown that oxygen chemisorption is the most important mechanistic step. However, as equilibrium is approached, desorption of SO_3 assumes considerable importance also.

These findings lead to the formulation of an improved rate equation, especially accurate near equilibrium for sulfur dioxide conversion. This is important in pollution abatement processing. The use of ^{35}S in developing improved catalysts is also suggested.

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SECTION I

CONCLUSIONS

Oxygen chemisorption is the most important mechanistic step in the catalytic oxidation of sulfur dioxide over vanadium pentoxide based catalyst.

Sulfur trioxide desorption rate is next in importance in control of the rate of oxidation of sulfur dioxide after oxygen chemisorption. Near equilibrium, it assumes almost the same importance as oxygen chemisorption.

The adsorption of sulfur dioxide and the chemical reaction between adsorbed sulfur dioxide and adsorbed oxygen both appear to be rapid steps, approaching equilibrium even at very low concentrations of SO_2 in the ambient gas.

Convenient rate equations for the speed of the overall conversion reaction may be developed on the basis of the previous findings. These should be useful in the design of both sulfuric acid plants and catalytic systems to remove SO_2 from stack gases.

In the case of sulfuric acid plants, the rate equation developed will enable assessment of the value of such processes as double adsorption of sulfur trioxide to increase overall sulfur dioxide conversion.

In both sulfuric acid plants and stack gas converters a more accurate prediction of catalyst requirement is possible for operation very close to equilibrium.

With the mechanistic information available the use of ^{35}S affords a convenient technique for evaluation of potential catalysts to determine their usefulness very close to equilibrium.

SECTION II

RECOMMENDATIONS

This program was limited to laboratory study and development of basic principles. It was not within the scope of the program to study the economics of improved designs of sulfuric acid plants based on optimizing procedures. Neither was it possible to evaluate various available catalysts thought to be promising in air pollution applications. It is recommended that both these programs be carried forward.

Designs of sulfuric acid plants very often employ rate equations which are not based on realistic information of reaction rates close to equilibrium. Since a very large proportion of the total catalyst volume in a reaction system is devoted to conversions of sulfur dioxide above the 95 percent level, it is apparent that sophisticated computational techniques must be supplemented by reliable assessment of catalyst behavior close to equilibrium. Tracer studies, such as are reported here, permit data of the required accuracy to be obtained. Available computer optimization studies should be reevaluated in the light of the information presented here.

As regards catalyst development, a number of ideas and new catalysts are available, but very little information is known about their performance close to equilibrium. Such data are of primary importance in minimizing atmospheric pollution. Thus a program of catalyst evaluation based on the tracer techniques developed here should be invaluable in selecting and formulating catalysts especially designed for high efficiency close to equilibrium.

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SECTION III

INTRODUCTION

The employment of isotopes has been shown to be useful in the study of heterogeneous catalytic systems.[1] Previous investigations have been confined, however, to situations in which a single rate controlling step is assumed to govern the mechanism which is followed in a complex reaction system. This procedure has shortcomings because it does not assess the relative importance of other significant factors which may be involved. The purpose of the present study was to explore the application of tracer techniques to define the important characteristics of the sulfur dioxide oxidation reaction. The study was limited to a commercial vanadium pentoxide based catalyst since this type is almost universally employed in commercial systems.

The first phase of the present study involved the application of ^{35}S as a tracer[2] to determine the possibility of the existence of more than a single rate controlling step. In this study it was found that steps involving sulfur account for some of the elementary reactions which are important in determining the overall reaction rate but that oxygen chemisorption appears to exert the major influence. Studies were therefore extended using ^{18}O as a tracer[3] in order to more reliably determine the influence of oxygen on the mechanism. From these studies it was possible to determine which of the steps in the reaction mechanism involving sulfur was responsible for influencing the overall reaction rate. The use of ^{18}O is more complicated than the use of ^{35}S because oxygen is present in all the terminal species involved. Therefore pertinent new theoretical development was necessary to interpret the data obtained.

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SECTION IV

THEORY

Results of these studies are interpreted on the basis of the following schematic representation for the mechanism of the overall reaction written as:

$$2\ SO_2 + O_2 \rightleftarrows 2\ SO_3 \qquad (1)$$

for modeling the system:

Step No.	Elementary reaction	Stoichiometric No., ν
1	$O_2 + 2\ell \underset{\nu_{-1}}{\overset{\nu_{+1}}{\rightleftharpoons}} 2\ O\ell$	1
2	$SO_2 + \ell \underset{\nu_{-2}}{\overset{\nu_{+2}}{\rightleftharpoons}} SO_2\ell$	2
3	$SO_2\ell + O\ell \underset{\nu_{-3}}{\overset{\nu_{+3}}{\rightleftharpoons}} SO_3\ell + \ell$	2
4	$SO_3\ell \underset{\nu_{-4}}{\overset{\nu_{+4}}{\rightleftharpoons}} SO_3 + \ell$	2

(2)

The stoichiometric number (ν) is defined as the number of times that each elementary step occurs for a single occurrence of the overall reaction as written. ℓ represents an active site associated with the catalyst. $O\ell$, $SO_2\ell$, and $SO_3\ell$ represent species obtained by reaction of the gaseous reactants and products with the catalyst. $\nu_{\pm i}$ represents velocities of individual mechanistic steps i = 1,2,3,4.

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This system may be exhibited in schematic form as:

$$\left.\begin{array}{l} SO_2 \underset{v_{-2}}{\overset{v_{+2}}{\rightleftharpoons}} SO_{2\ell} \\ O_2 \underset{v_{-1}}{\overset{v_{+1}}{\rightleftharpoons}} O_{\ell} \end{array}\right\} \underset{v_{-3}}{\overset{v_{+3}}{\rightleftharpoons}} SO_{3\ell} \underset{v_{-4}}{\overset{v_{+4}}{\rightleftharpoons}} SO_3 \qquad (3)$$

One relationship between the velocities involved may be obtained from thermodynamics and transition state theory as discussed by Csuha and Happel.[4] For each individual step in Equation (2) the following relationship may be written:

$$\Delta g_i = - RT \ln \frac{v_{+i}}{v_{-i}} \qquad (4)$$

where Δg_i is the Gibbs free energy for a single mechanistic step, R is the universal gas constant, and T is the absolute temperature. The total Gibbs free energy change ΔG for the complete reaction is the sum of the free energies for all elementary steps multiplied by the stoichiometric number of each step:

$$\Delta G = \Delta g_1 + 2\,\Delta g_2 + 2\,\Delta g_3 + 2\,\Delta g_4 \qquad (5)$$

Hence, combining Equations (4) and (5), we may write:

$$\text{Exp}\ (-\Delta G/RT) = \left(\frac{v_{+1}}{v_{-1}}\right)\left(\frac{v_{+2}\ v_{+3}\ v_{+4}}{v_{-2}\ v_{-3}\ v_{-4}}\right)^2 \qquad (6)$$

The squared term appears for the v_{+2}, v_{+3}, and v_{+4} velocities because the stoichiometric number for these steps is 2.

For the catalytic oxidation of sulfur dioxide the Gibbs free energy change is:

$$\Delta G = RT \ln \left[\frac{P_{SO_3}^{\ 2}}{P_{SO_2}^{\ 2} P_{O_2} K\rho} \right] \qquad (7)$$

$K\rho$ is the equilibrium constant; and P_{SO_3}, P_{SO_2}, and P_{O_2} are the partial pressures of the species involved. In the non-ideal case the partial pressures would be replaced by the partial fugacities.

^{35}S data enables the velocity ratio in the sulfur path[2] to be determined. The sulfur path represents velocities of atomic sulfur transfer in the forward $V_+^{2,3,4}$ and backward $V_-^{2,3,4}$ directions (see Equation (3)). It is related to the individual step velocities by the equation:[1]

$$\frac{V_+^{2,3,4}}{V_-^{2,3,4}} = \frac{v_{+2}\, v_{+3}\, v_{+4}}{v_{-2}\, v_{-3}\, v_{-4}} \qquad (8)$$

By using Equations (6) and (8) it is thus possible to determine the velocity ratio v_{+1}/v_{-1} for given reaction conditions.

The transfer of oxygen is more complicated[3] and requires two levels of marking with oxygen for the determination of:

$$\frac{V_+^{1,3,4}}{V_-^{1,3,4}} = \frac{v_{+1}\, v_{+3}\, v_{+4}}{v_{-1}\, v_{-3}\, v_{-4}} \qquad (9)$$

However, in this case it is possible to determine v_{+4}/v_{-4} as well. Sufficient information is then available to solve also for v_{+2}/v_{-2} and v_{+3}/v_{-3} so that estimates are available for velocity ratios of all steps of the model.

It is often convenient to report the values obtained in terms of the apparent stoichiometric number. If the tracer follows the rate controlling step or steps, the apparent stoichiometric number will correspond to the true stoichiometric number of the step or steps involved. Thus if the rate controlling steps were in the sulfur path, $v_{+1}/v_{-1} = 1$ because oxygen chemisorption would be at equilibrium. Then from Equation (6), we would have:

$$2 = \frac{-\Delta G/RT}{\ln \frac{v_{+2}\, v_{+3}\, v_{+4}}{v_{-2}\, v_{-3}\, v_{-4}}} \qquad (10)$$

In general, if the ratio in Equation (10) were not equal to 2, it would still be possible to compute an apparent stoichiometric number which would indicate the departure of the system from rate control by steps in the sulfur path. When ^{35}S is used as a tracer to follow the atomic velocity of sulfur in the path through steps 2, 3, and 4 in Equation (2), the apparent stoichiometric number can be expressed as:

$$\nu_S = \frac{-\Delta G/RT}{\ln \frac{v_+^{2,3,4}}{v_-^{2,3,4}}} \qquad (11)$$

The value $-\Delta G/RT$ can be computed from Equation (7), while the ratio $v_+^{2,3,4}/v_-^{2,3,4}$ is available from the ^{35}S tracer data. A value of $\nu_S \cong 2$ indicates that either step 2,3, or 4 in Equation (2) is rate controlling. On the other hand, a value of $\nu_S > 2$ is evidence that oxygen chemisorption exerts an effect on the overall rate. Similar relationships are possible using ^{18}O as a tracer, but then two apparent stoichiometric numbers are obtainable: oxygen can follow either steps 2,3, and 4 like sulfur, or steps 1,3, and 4.

SECTION V

EXPERIMENTAL RESULTS

A recirculating reactor is used in this study to minimize diffusional and temperature gradients exterior to the particles. A full description of the equipment is given elsewhere.[2] Feed and product gases are analyzed by gas chromatographic techniques.[5,6]

Sulfur dioxide tagged with ^{35}S and sulfur dioxide and oxygen tagged with ^{18}O were obtained from New England Nuclear Corp. A Model Unilux II (Nuclear Chicago Corp.) scintillation counter was used to analyze for ^{35}S. ^{18}O content of SO_2 and O_2 was determined by a Type 21-103C mass spectrometer (Consolidated).

A special technique was used to determine the degree of ^{18}O tagging in sulfur trioxide. Sulfur trioxide and sulfur dioxide were condensed from the effluent in an acetone dry-ice bath and the mixture was subsequently cracked at 1000°C in a platinum catalyst reactor. The SO_2 and O_2 produced were analyzed for ^{18}O by mass spectrometer. The ^{18}O content of the SO_3 was then calculated by performing a mass balance.

The catalyst employed was a commercial vanadium pentoxide based catalyst (typical analysis V_2O_5 -- 9.1 wt %; K_2O -- 10.1 wt %) supplied by American Cyanamid Co. Catalyst pellets were crushed and screened to a size range of 0.35 - 0.71 mm. Data obtained previously[2] indicated that diffusional effects are not important under the present experimental conditions.

Table 1 summarizes data for several different reaction conditions, all at temperatures of 470-480°C using ^{18}O as a tracer.[3,7] About 80 percent N_2 was employed as a diluent in these experiments. The partial pressure of SO_2 was maintained at a low value of 0.003 - 0.005 atm and

Table 1. TRACER DATA USING ^{18}O

Run No.	$(V_+/V_-)^{1,3,4}$	$(V_+/V_-)^{2,3,4}$	v+1/v-1	v+2/v-2	v+3/v-3	v+4/v-4	(v+2/v-2)/(v+3/v-3)	exp(-ΔG/RT)
4	4.453	1.431	4.604	1.479	0.585	1.653	0.866	9.425
7	4.453	1.431	4.095	1.316	0.938	1.160	1.245	8.384
11	2.138	1.356	1.860	1.179	0.963	1.194	1.135	3.418
12	2.138	1.356	2.624	1.664	0.668	1.221	1.111	4.823
13	6.785	1.545	5.090	1.159	1.093	1.220	1.267	12.155
14	6.785	1.545	3.843	0.875	0.943	1.872	0.826	9.177
15	3.52	1.303	4.65	1.721	0.584	1.297	1.004	7.891
16	3.52	1.303	3.439	1.273	0.914	1.119	1.164	5.837
16[a]	3.742	1.520	3.840	1.560	0.806	1.208	1.258	5.837
23	24.838	1.469	15.575	0.921	1.130	1.411	1.041	33.630
24	24.838	1.469	7.431	0.440	2.292	1.458	1.008	16.045
23[a]	24.156	1.392	17.353	1.000	1.020	1.365	1.020	33.630
24[a]	13.568	1.327	9.116	0.891	1.283	1.160	1.143	16.045
25[a]	1.570	1.276	1.896	1.181	0.853	1.271	1.0035	2.357

[a] Using ^{35}S data.

equilibrium was approached essentially by employment of different partial pressures of O_2 and SO_3.

Figure 1 presents the same information in a plot of velocity ratios. Details of the original data and calculation procedure are given in Appendix A. The velocity ratios for steps 2 and 3 are combined as the product (v_{+2}/v_{-2}) (v_{+3}/v_{-3}) because their individual determination is less accurate than (v_{+4}/v_{-4}). For a step or combination of steps at equilibrium the velocity ratio will be equal to unity. From examination of Figure 1, it appears that steps 2 and 3 are close to equilibrium. In step 4, SO_3 desorption is a factor in determination of the overall rate, especially close to equilibrium for the overall reaction. Oxygen chemisorption is always the slowest step and farthest from equilibrium.

Since the ^{18}O tracer experiments indicate that steps 2 and 3 are at equilibrium, the use of ^{35}S permits the direct determination of the velocity ratio v_{+4}/v_{-4}. This constitutes a considerable simplification in the experimental procedure since ^{35}S data are reasonably easy to acquire.

Figure 2 is a plot of apparent stoichiometric numbers obtained using ^{35}S. Data are tabulated in Table 2. Further details are in references (2) and (7). Although there is some scatter in the data, it appears that near equilibrium for the overall reaction, at the lowest partial pressure ratios of p_{SO_2}/p_{O_2}, the apparent stoichiometric number in the sulfur path corresponds to $\nu_S = 3.38 \pm 0.21$. Since the apparent stoichiometric number is greater than 2, both SO_3 desorption and O_2 chemisorption are not at equilibrium and affect the overall reaction rate. The next section shows how this information can be employed to develop an improved rate expression for conditions approaching equilibrium for the overall reaction.

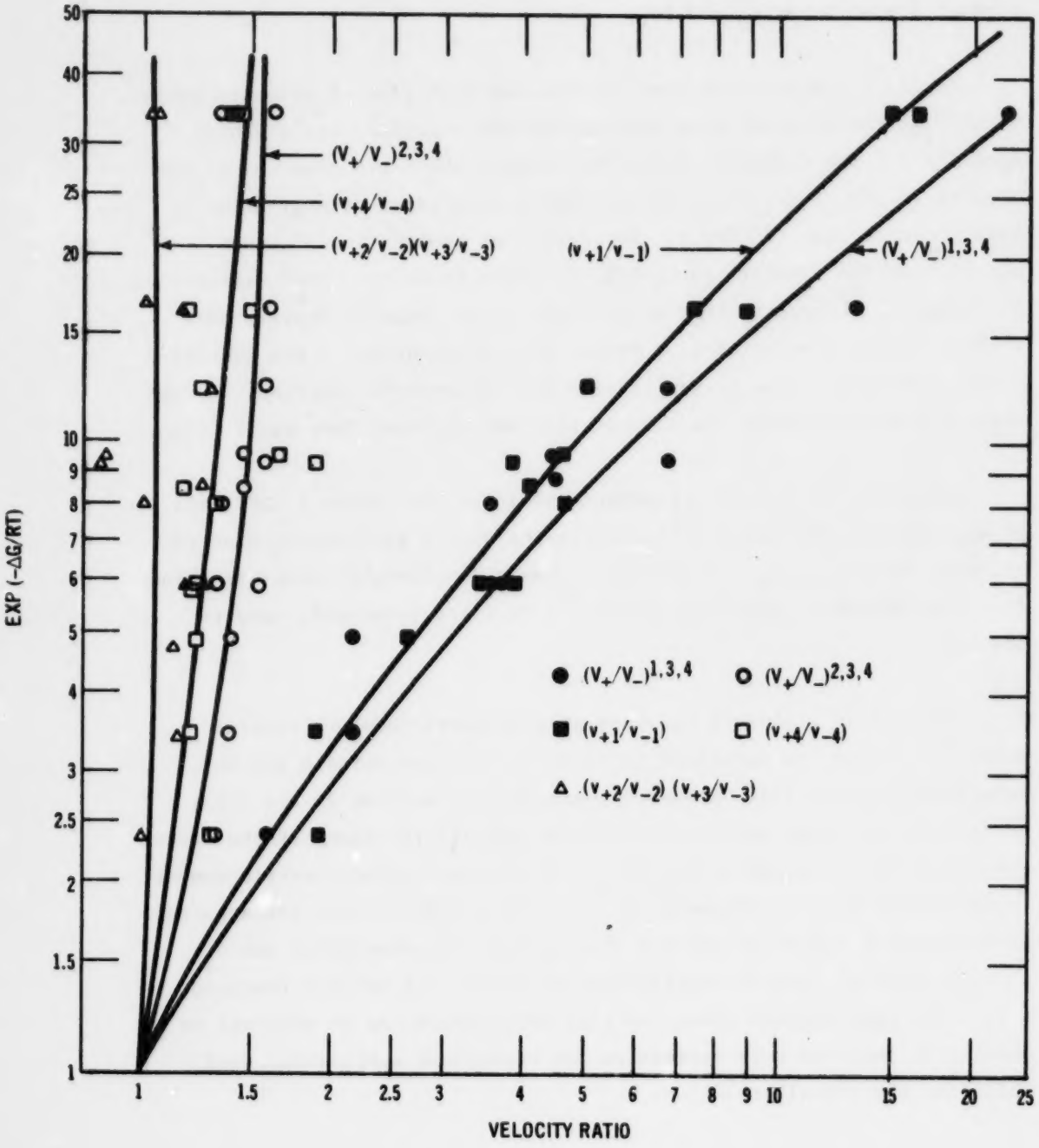

Figure 1. Velocity ratios for SO_2 oxidation.

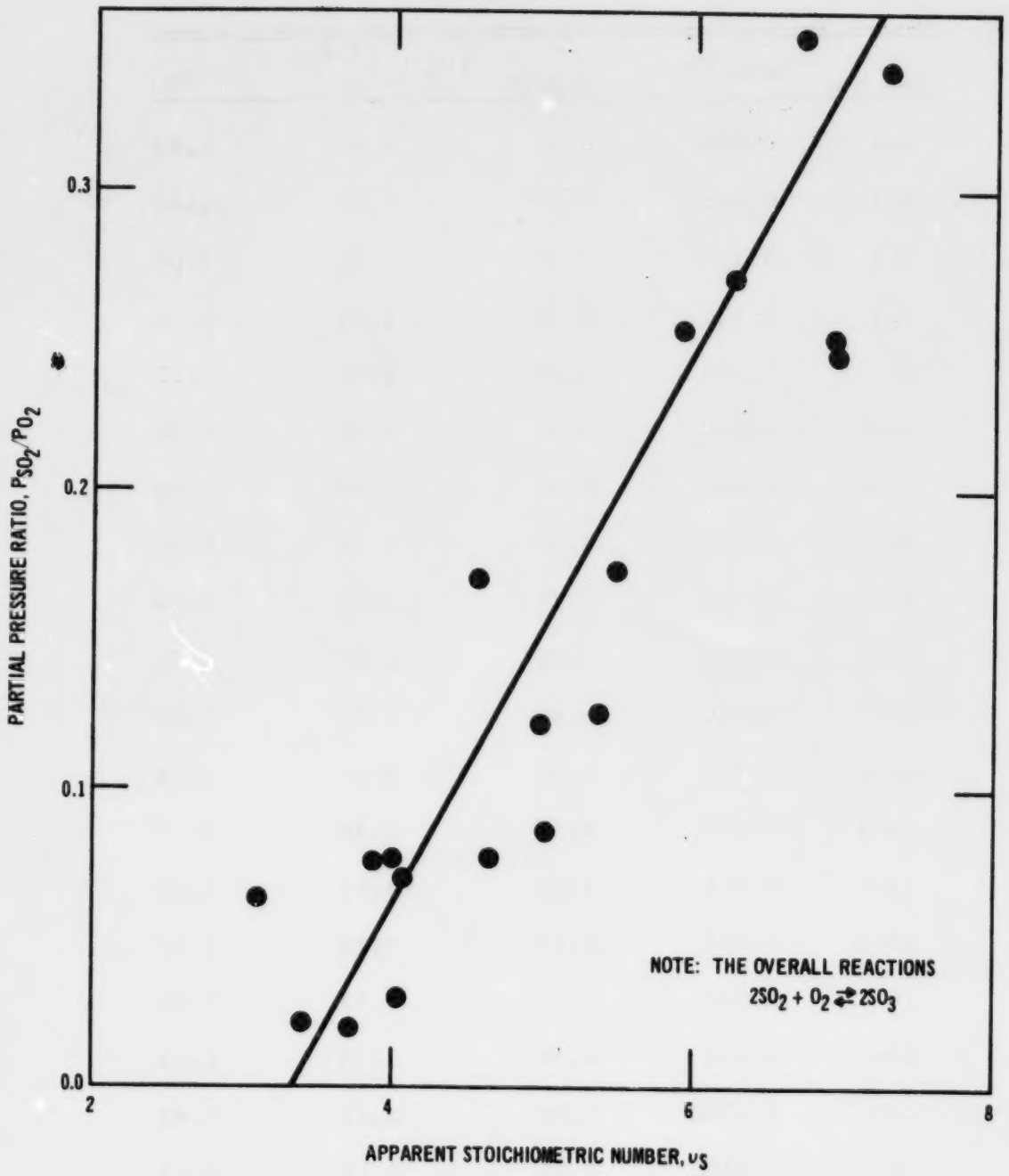

Figure 2. Sulfur tracer data.

Table 2. SULFUR TRACER DATA

Run No.	P_{SO_2}/P_{O_2}	$-\Delta G/RT$	$(V_+/V_-)_S^{2,3,4}$	ν_S
4-1	0.250	8.12	3.22	6.94
4-2	0.246	8.00	3.16	6.96
5-1	0.122	5.12	2.78	5.00
5-2	0.126	5.22	2.64	5.38
6	0.065	3.58	3.06	3.12
9-2	0.336	10.18	4.40	6.88
10-1	0.255	7.56	3.56	5.94
10-2	0.270	7.90	3.52	6.28
12-1	0.165	5.58	3.37	4.58
12-2	0.174	5.76	2.84	5.50
13	0.087	3.58	2.03	5.04
14-1	0.071	3.60	2.16	4.64
14-2	0.071	3.56	2.38	4.10
15-1	0.077	3.26	2.32	3.88
15-2	0.077	3.24	2.24	4.02
16	0.340	9.60	3.73	7.28
17-1	0.335	8.94	3.58	7.02
19-1	0.0208	2.92	2.35	3.42
19-2	0.0208	2.92	2.18	3.74
20	0.0066	-	-	3.30

SECTION VI

IMPROVED RATE EQUATION

It is possible to derive a rate equation which is applicable to near equilibrium conditions by making use of this information. Since Equations (2) and (3) are at equilibrium, and therefore $v_{+2}/v_{-2} = v_{+3}/v_{-3} = 1$, we may write:

$$\frac{V_+^{1,3,4}}{V_-^{1,3,4}} = \left[\frac{v_{+1}}{v_{-1}}\right]\left[\frac{v_{+4}}{v_{-4}}\right] \tag{12}$$

But from Equation (6) we have:

$$\exp\left(-\Delta G/RT\right) = \left[\frac{v_{+1}}{v_{-1}}\right]\left[\frac{v_{+4}}{v_{-4}}\right]\left[\frac{v_{+4}}{v_{-4}}\right] \tag{13}$$

Now as previously noted (see Equation (11)):

$$\exp\left(\frac{-\Delta G}{\nu_S RT}\right) = \frac{v_{+4}}{v_{-4}} \tag{14}$$

Substituting values from Equations (12) and (14) into (13), we obtain:

$$\frac{V_+^{1,3,4}}{V_-^{1,3,4}} = \left[-\frac{\Delta G}{RT}\right]\left[1 - \frac{1}{\nu_S}\right] \tag{15}$$

Using the relationship $V = V_+^{1,3,4} - V_-^{1,3,4}$, we obtain the rate expression:

$$V = V_+^{1,3,4}\left[1 - \left(e^{-\Delta G/RT}\right)^{(\nu_S - 1)/\nu_S}\right] \tag{16}$$

Since the potential term influences behavior only near equilibrium, it is probably a good approximation to employ the limiting form of the exponent $(\nu_S-1)/\nu_S$ in Equation (16). More accurate representations would be possible, if desired.

The forward velocity V_+[1,3,4] could be established by experimentation far from equilibrium, which is usually the case for studies reported in the literature. A suitable form of forward reaction velocity based on a careful experimental study is given by Simecek et al.[8] If this is incorporated into Equation (12), together with the results we have obtained to assign the value $(\nu_S-1)/\nu_S = 0.704$, the resulting rate equation is:

$$V = \frac{k\,K\,p_{SO_3}\,p_{O_2}}{\left[p_{SO_3}^{1/2} + (K\,p_{SO_2})^{1/2}\right]^2}\left[1 - \left(\frac{p_{SO_3}^2}{p_{SO_2}^2\,p_{O_2}\,K_p}\right)^{0.704}\right] \quad (17)$$

Since the data of Simecek et al. were obtained with a different vanadium pentoxide catalyst than that employed in this study, values should not be assigned to the constants k and K. Use of the exponent 0.704, however, does substantially improve the agreement of the correlation of Simecek's data near equilibrium using Equation (17). We did not have the opportunity to develop the appropriate constants for the Cyanamid catalyst because the present investigation was terminated due to more pressing goals.

The basic procedure is straightforward and it seems clear that the employment of Equation (12) should effect substantial improvement in the correlation of sulfur dioxide oxidation data.

SECTION VII

DISCUSSION

Rate Equation (13) represents a new approach to the development of kinetic relationships near equilibrium. By using ^{35}S data it is possible to independently assess the importance of the sulfur trioxide desorption step close to equilibrium. Previous relationships have all been based on the assumption that one step is rate controlling, either a step in the sulfur path or more frequently oxygen chemisorption.

Aside from the development of an improved rate expression, the use of ^{35}S should constitute a sensitive method for catalyst evaluation near equilibrium. It is possible that an improved catalyst formulation will be possible by this more discriminating experimental procedure which enables the relative importance of oxygen chemisorption and SO_3 desorption to be estimated.

SECTION VIII

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SECTION IX

PUBLICATIONS

References 2, 3, and 4 were published directly as a result of the project.

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APPENDIX A

OXYGEN TAGGING

Table A-1 summarizes the calculated data plotted in Figure 1. In this table the tracer data are as reported in terms of a notation given by Csuha and Happel:[4]

$$t_e^{\,d} = \frac{\left[\begin{array}{l}\text{net rate at which tagged atoms of e}\\ \text{leave a reactant or enter a product}\\ \text{species (gm atoms per hour per gm}\\ \text{of catalyst)}\end{array}\right]}{\left[\begin{array}{l}\text{number of atoms}\\ \text{of e in a molecule}\\ \text{of species d}\end{array}\right]\left[\begin{array}{l}\text{coefficient of the species}\\ \text{d in the chemical equation}\\ \text{of the overall reaction}\end{array}\right]}$$

$$z_e^{\,d} = \text{fraction of tagged atoms e in species d}$$

The following discussion gives details of the method of calculation to obtain the results presented in Table 1 of the main body of the report for oxygen tracing. There are three tagged atomic velocities for oxygen ($t_0^{\,O_2}$, $t_0^{\,SO_2}$, and $t_0^{\,SO_3}$), which are restricted by stoichiometry such that:

$$t_0^{\,SO_3} = \frac{1}{3}\, t_0^{\,O_2} + \frac{2}{3}\, t_0^{\,SO_2} \qquad \text{(A-1)}$$

Here the subscript 0 denotes atomic oxygen. The tagged atomic velocities t_e may be derived by material balances as:

$$t_0^{\,O_2} = z_0^{\,O_2}\, v_{+1} - z_0^{\,O_2\ell}\, v_{-1} \qquad \text{(A-2)}$$

$$t_0^{\,SO_2} = (z_0^{\,SO_2}\, v_{+2} - z_0^{\,SO_2\ell}\, v_{-2})/2 \qquad \text{(A-3)}$$

$$t_0^{\,O_2} = (z_0^{\,O\ell}\, v_{+3} - z_0^{\,SO_3\ell}\, v_{-3})/2 \qquad \text{(A-4)}$$

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$$t_0^{SO_2} = (z_0^{SO_2\ell}\ v_{+3} - z_0^{SO_3\ell}\ v_{-3})/2 \qquad \text{(A-5)}$$

$$t_0^{SO_3} = (z_0^{SO_3\ell}\ v_{+4} - z_0^{SO_3}\ v_{-4})/2 \qquad \text{(A-6)}$$

Since it is not possible to measure the concentrations of isotopic surface fractions on the catalyst, they must be eliminated. Substitution of values for $z_0^{O\ell}$ and $z_0^{SO_3\ell}$ from Equations (A-2) and (A-6) yields the relationship:

$$z_0^{SO_3} = z_0^{O_2}\left[\frac{v_{+1}\ v_{+3}\ v_{+4}}{v_{-1}\ v_{-3}\ v_{-4}}\right] - t_0^{SO_3}\left(\frac{2}{v_{-4}}\right) - t_0^{O_2}\left[\frac{2\ v_{+4}}{v_{-3}v_{-4}} + \frac{v_{+3}\ v_{+4}}{v_{-1}v_{-3}v_{-4}}\right] \qquad \text{(A-7)}$$

Similarly, elimination of the isotopic surface fractions from Equations (A-3), (A-5), and (A-6) yields the expression:

$$z_0^{SO_3} = z_0^{SO_2}\left[\frac{v_{+2}\ v_{+3}\ v_{+4}}{v_{-2}\ v_{-3}\ v_{-4}}\right] - t_0^{SO_3}\left(\frac{2}{v_{-4}}\right) - t_0^{SO_2}\left[\frac{2\ v_{+4}}{v_{-3}v_{-4}} + \frac{2\ v_{+3}\ v_{+4}}{v_{-2}v_{-3}v_{-4}}\right] \qquad \text{(A-8)}$$

From previous studies,[1,4] the following relationships are available for the combined path velocities in terms of individual steps:

$$\frac{V_+^{1,3,4}}{V_-^{1,3,4}} = \frac{v_{+1}\ v_{+3}\ v_{+4}}{v_{-1}\ v_{-3}\ v_{-4}} \qquad \text{(A-9)}$$

$$\frac{V_+^{2,3,4}}{V_-^{2,3,4}} = \frac{v_{+2}\ v_{+3}\ v_{+4}}{v_{-2}\ v_{-3}\ v_{-4}} \qquad \text{(A-10)}$$

$$\frac{1}{V_{-}^{1,3,4}} = \frac{2}{v_{-4}} + \frac{2\,v_{+4}}{v_{-4}v_{-3}} + \frac{v_{+4}\,v_{+3}}{v_{-4}v_{-3}v_{-1}} \qquad \text{(A-11)}$$

$$\frac{1}{V_{-}^{2,3,4}} = \frac{2}{v_{-4}} + \frac{2\,v_{+4}}{v_{-4}v_{-3}} + \frac{2\,v_{+4}v_{+3}}{v_{-4}v_{-3}v_{-2}} \qquad \text{(A-12)}$$

Using these relationships, Equations (A-7) and (A-8) may be expressed as:

$$z_0^{SO_3} = z_0^{SO_2}\left(\frac{V_{+}^{1,3,4}}{V_{-}^{1,3,4}}\right) - \frac{t_0^{O_2}}{V_{-}^{1,3,4}} + \frac{2}{v_{-4}}\,(t_0^{O_2} - t_0^{SO_3}) \qquad \text{(A-13)}$$

$$z_0^{SO_3} = z_0^{SO_2}\left(\frac{V_{+}^{2,3,4}}{V_{-}^{2,3,4}}\right) - \frac{t_0^{SO_2}}{V_{-}^{2,3,4}} + \frac{2}{v_{-4}}\,(t_0^{SO_2} - t_0^{SO_3}) \qquad \text{(A-14)}$$

The velocity in a path is related to the overall velocity by:

$$V = V_{+}^{2,3,4} - V_{-}^{2,3,4} = V_{+}^{1,3,4} - V_{-}^{1,3,4} \qquad \text{(A-15)}$$

Use of this relationship gives:

$$\frac{V_{+}^{1,3,4}}{V_{-}^{1,3,4}}\,(t_0^{O_2} - V\,z_0^{O_2}) = t_0^{O_2} - V\,z_0^{SO_3} + \frac{2V}{v_{-4}}(t_0^{O_2} - t_0^{SO_3}) \qquad \text{(A-16)}$$

$$\frac{V_{+}^{2,3,4}}{V_{-}^{2,3,4}}\,(t_0^{SO_2} - V\,z_0^{SO_2}) = t_0^{SO_2} - V\,z_0^{SO_3} + \frac{2V}{v_{-4}}\,(t_0^{SO_2} - t_0^{SO_3}) \qquad \text{(A-17)}$$

The overall velocity of a complex chemical reaction can also be represented in terms of the forward and backward velocities of the steps in the mechanism as:

$$V = (v_{+i} - v_{-i})/v_i \qquad \text{(A-18)}$$

Thus for step 4:

$$V = (v_{+4} - v_{-4})/v_4 = (v_{+4} - v_{-4})/2 \qquad \text{(A-19)}$$

This equation can be rewritten as:

$$\frac{2V}{v_{-4}} = \frac{v_{+4}}{v_{-4}} - 1 \qquad \text{(A-20)}$$

By use of Equations (A-20) and (A-1), Equations (A-16) and (A-17) can be further simplified to obtain:

$$\frac{v_+^{1,3,4}}{v_-^{1,3,4}} (t_0{}^{O}2 - V\, z_0{}^{O}2) = t_0{}^{O}2 - V\, z_0{}^{SO}3 + \frac{2}{3}\left(\frac{v_{+4}}{v_{-4}} - 1\right)(t_0{}^{O}2 - t_0{}^{SO}2) \qquad \text{(A-21)}$$

$$\frac{v_+^{2,3,4}}{v_-^{2,3,4}} (t_0{}^{SO}2 - V\, z_0{}^{SO}2) = t_0{}^{SO}2 - V\, z_0{}^{SO}3 - \left(\frac{1}{3}\frac{v_{+4}}{v_{-4}} - 1\right)(t_0{}^{O}2 - t_0{}^{SO}2) \qquad \text{(A-22)}$$

If Equation (A-22) is multiplied by 2 and subtracted from (A-21), the following relationship is obtained:

$$\frac{V_+^{1,3,4}}{V_-^{1,3,4}} (t_0{}^{0}2 - V\, z_0{}^{0}2) + 2\, \frac{V_+^{2,3,4}}{V_-^{2,3,4}} (t_0{}^{SO}2 - V\, z_0{}^{SO}2) = 2\, t_0{}^{SO}2 + t_0{}^{0}2 - 3\, V\, z_0{}^{SO}3 \qquad \text{(A-23)}$$

Now, since Equation (A-23) has two unknown quantities -- $(V_+/V_-)^{1,3,4}$ and $(V_+/V_-)^{2,3,4}$ -- experiments with two levels of marking at a given overall V using ^{18}O as a tracer will establish the values of these velocity ratios. Once they are obtained, substitution into Equation (A-21) or (A-22) will provide a value for v_{+4}/v_{-4}.

The following equation appears as Equation (6) in the main body of the report:

$$\text{Exp} - \frac{\Delta G}{RT} = \left(\frac{v_{+1}}{v_{-1}}\right) \left(\frac{v_{+2}}{v_{-2}} \frac{v_{+3}}{v_{-3}} \frac{v_{+4}}{v_{-4}}\right)^2 \qquad \text{(A-24)}$$

From Equations (A-10) and (A-24), the relationship to calculate v_{+1}/v_{-1} is obtained:

$$\frac{v_{+1}}{v_{-1}} = \frac{\text{Exp}\left(-\frac{\Delta G}{RT}\right)}{\left(\frac{V_+^{2,3,4}}{V_-^{2,3,4}}\right)^2} \qquad \text{(A-25)}$$

From previously computed values of (v_{+4}/v_{-4}) and $(V_+/V_-)^{1,3,4}$, and Equation (A-9), the value of (v_{+3}/v_{-3}) may be computed as:

$$\frac{v_{+3}}{v_{-3}} = \frac{\frac{V_+^{1,3,4}}{V_-^{1,3,4}}}{\left(\frac{v_{+1}}{v_{-1}}\right)\left(\frac{v_{+4}}{v_{-4}}\right)} \qquad \text{(A-26)}$$

Finally, from the previously calculated values and Equation (A-10), v_{+2}/v_{-2} is obtained:

$$\frac{v_{+2}}{v_{-2}} = \frac{\frac{V_+^{2,3,4}}{V_-^{2,3,4}}}{\left(\frac{v_{+3}}{v_{-3}}\right)\left(\frac{v_{+4}}{v_{-4}}\right)} \qquad \text{(A-27)}$$

As an example of the application of this procedure, consider the data from runs 23 and 24 in Table A-1. In order to solve Equation (A-23), we will first compute the following coefficients from run 23:

$$t_0{}^{O_2} - V z_0{}^{O_2} = (1.3828 - 12.292\ (0.10687)) \times 10^{-4}$$

$$= \underline{0.06914 \times 10^{-4}}$$

$$t_0{}^{SO_2} - V z_0{}^{SO_2} = (-0.15167 - 12.292\ (0.012459)) \times 10^{-4}$$

$$= \underline{-0.30481 \times 10^{-4}}$$

$$2\, t_0{}^{SO_2} + t_0{}^{O_2} - 3V z_0{}^{SO_3} = (2(-0.15167) + 1.3828 - 3(12.292)\ (0.006998)) \times 10^{-4}$$

$$= \underline{0.82142 \times 10^{-4}}$$

Upon substitution of these values into Equation (A-23), we obtain:

$$-(V_+/V_-)^{1,3,4} + 8.8177\ (V_+/V_-)^{2,3,4} = -11.8812 \qquad \text{(A-28)}$$

A similar computation of the data in Table A-1 for run 24, under overall velocity conditions similar to run 23, gives the following, upon substitution into Equation (A-23):

$$- (V_+/V_-)^{1,3,4} + 78.9419\ (V_+/V_-)^{2,3,4} = 91.1601 \qquad \text{(A-29)}$$

Simultaneous solution of Equations (A-28) and (A-29) gives the following values of the overall velocity ratios:

$$(V_+/V_-)^{2,3,4} = 1.4694$$

$$(V_+/V_-)^{1,3,4} = 24.8380$$

The overall velocity ratios are used to calculate v_{+1}/v_{-1} using Equation (A-25). Thus for run 23:

$$\frac{v_{+1}}{v_{-1}} = \frac{33.63}{(1.4694)^2} = \underline{15.575}$$

For run 23, v_{+4}/v_{-4} may be calculated by Equation (A-22), using the following values of coefficients:

$$t_0{}^{SO}{}_2 - V\, z_0{}^{SO}{}_2 = (-0.15167 - 12.2918\ (0.012459)) \times 10^{-4}$$

$$= \underline{- 0.30481 \times 10^{-4}}$$

$$t_0{}^{SO}{}_2 - V\, z_0{}^{SO}{}_3 = (- 0.15167 - 12.2918\ (0.006998)) \times 10^{-4}$$

$$= \underline{- 0.23779 \times 10^{-4}}$$

$$t_0{}^{O}{}_2 - t_0{}^{SO}{}_2 = (1.3828 + 0.15167) \times 10^{-4}$$

$$= \underline{1.5345 \times 10^{-4}}$$

and $v_{+4}/v_{-4} = \underline{1.4110}$

The velocity ratio for step 3 will be:

$$v_{+3}/v_{-3} = \frac{(V_+/V_-)^{1,3,4}}{(v_{+1}/v_{-1})\ (v_{+4}/v_{-4})} = \frac{24.838}{(15.575)\ (1.4110)} = \underline{1.1302}$$

Finally the velocity ratio for step 2 is:

$$v_{+2}/v_{-2} = \frac{(V_+/V_-)^{2,3,4}}{(v_{+3}/v_{-3})\ (v_{+4}/v_{-4})} = \frac{1.4694}{(1.1302)\ (1.4110)} = \underline{0.9214}$$

Note that additional values for runs 23 and 24 appear in Table A-1 based on values for $(V_+/V_-)^{2,3,4}$ using ^{35}S tracing simultaneously with ^{18}O tracing. In this case it is only necessary to substitute the value of $(V_+/V_-)^{2,3,4}$ into Equation (A-23) and solve directly for $(V_+/V_-)^{1,3,4}$. Two simultaneous equations are not required as in the case of ^{18}O tracing alone.

Table A-1. TRACER DATA USING ^{18}O

Run No.	2	3	4	7	8	9	10	11
Wt of catalyst, grams	0.3956	0.3956	0.7941	0.7941	0.7941	0.7941	0.7941	0.7941
Reaction press., atm	1.0496	1.0870	1.0632	1.0490	1.0534	1.0647	1.0647	1.0440
Reaction temp, ^{o}C	472	470	472	476	474	476	478	476
P_{N_2}, atm	0.8258	0.8152	0.8177	0.8233	0.9097	0.9160	0.9240	0.9451
P_{O_2}, atm	0.1773	0.2300	0.2001	0.1806	0.0977	0.0444	0.0388	0.0585
$P_{SO_2} \times 10^2$, atm	2.6220	2.3180	0.3195	0.3418	0.5682	8.3003	7.0434	0.3474
P_{SO_3}, atm	0.0203	0.0186	0.0422	0.0417	0.0403	0.0213	0.0315	0.0369
P_{SO_2}/P_{O_2}	0.148	0.101	0.016	0.019	0.058	1.871	1.818	0.059
$V \times 10^3$, g mol/ g cat. hr	10.49	14.598	1.476	2.580	2.381	6.641	8.864	1.152
$t_0^{O2} \times 10^4$	1.6165	7.2388	-0.1951	0.0514	0.0678	-1.9694	11.450	1.0423
$t_0^{SO2} \times 10^4$	14.1262	-0.2043	1.4980	1.2854	1.5512	3.8679	3.782	-0.0318
$t_0^{SO3} \times 10^4$	9.9561	2.3007	0.9636	0.8782	1.0567	1.9220	6.344	0.3262
$z_0^{O2} \times 10^2$	3.649	4.495	0.235	0.448	0.644	0.572	12.960	4.321
$z_0^{SO2} \times 10^2$	3.178	0.270	1.738	1.880	4.524	3.084	2.819	0.481
$z_0^{SO3} \times 10^2$	3.849	1.508	0.613	0.797	1.709	1.437	3.050	0.148
$K \times 10^{-3}$, atm^{-1}	8.20	9.00	8.23	6.90	7.55	6.90	6.30	6.90
$-\Delta G/RT$	7.795	8.078	2.245	2.103	2.687	8.450	7.130	1.228
$\exp(-\Delta G/RT)$	2424	3219	9.425	8.384	14.684	4.641	1248.5	3.418

Table A-1 (continued). TRACER DATA USING ^{18}O

Run No.	12	13	14	15	16	17	18	19
Wt of catalyst, grams	0.7941	0.7941	0.7941	0.7494	0.7494	0.7494	0.7494	0.7494
Reaction press., atm	1.0440	1.0750	1.0750	1.0603	1.0603	1.0645	1.0633	1.0633
Reaction temp, ^oC	480	475	475	477	480	478	478	479
P_{N_2}, atm	0.9408	1.0377	1.0354	1.0170	1.0152	0.9657	0.9521	0.9552
P_{O_2}, atm	0.0620	0.0183	0.0192	0.0215	0.0222	0.0595	0.0684	0.0657
$P_{SO_2} \times 10^2$, atm	0.4295	0.4410	0.4535	0.4139	0.4026	0.2340	0.3328	0.3474
P_{SO_3}, atm	0.0373	0.0145	0.0158	0.0175	0.0189	0.0369	0.0395	0.0389
P_{SO_2}/P_{O_2}	0.069	0.241	0.236	0.193	0.182	0.039	0.049	0.053
$V \times 10^3$, g mol/ g cat. hr	1.152	1.434	1.828	1.984	1.639	1.651	1.503	1.339
$t_0^{O_2} \times 10^4$	1.0584	4.4787	-0.0927	-0.1100	4.0981	2.7536	-0.00921	-0.0721
$t_0^{SO_2} \times 10^4$	0.7024	-0.3479	1.5953	1.8090	-0.2951	0.1522	0.7842	0.3792
$t_0^{SO_3} \times 10^4$	0.8164	1.3081	0.9069	1.1694	2.4315	1.0193	0.5205	0.2288
$z_0^{O_2} \times 10^2$	4.850	26.088	0.492	0.421	17.837	13.013	0.263	0.284
$z_0^{SO_2} \times 10^2$	2.039	1.578	1.929	2.123	1.854	1.427	3.540	2.732
$z_0^{SO_3} \times 10^2$	0.369	1.298	1.010	0.963	1.893	0.673	0.348	0.405
$K \times 10^{-3}$, atm^{-1}	5.75	7.20	7.20	6.60	5.78	6.30	6.30	6.05
$-\Delta G/RT$	1.572	2.495	2.205	2.064	1.765	0.410	1.120	1.154
$\exp(-\Delta G/RT)$	4.823	12.155	9.177	7.891	5.837	1.507	3.061	3.171

Table A-1 (continued). TRACER DATA USING ^{18}O

Run No.	20	21	22	23	24	25
Wt of catalyst, grams	0.7494	0.7494	0.7494	0.7505	0.7505	0.7502
Reaction press., atm	1.0453	1.0466	1.0453	1.0549	1.0558	1.0612
Reaction temp, ^{o}C	481	479	481	477	477	478
P_{N_2}, atm	1.0125	1.0051	1.0127	1.0147	1.0160	1.0239
P_{O_2}, atm	0.0110	0.0203	0.0108	0.0223	0.0216	0.0239
$P_{SO_2} \times 10^2$, atm	0.5416	0.5628	0.5229	0.579	0.456	0.1505
P_{SO_3}, atm	0.0164	0.0156	0.0166	0.0121	0.0136	0.0120
P_{SO_2}/P_{O_2}	0.492	0.278	0.487	0.260	0.211	0.063
$V \times 10^3$, g mol/ g cat. hr	1.240	1.708	1.127	1.229	1.458	0.218
$t_0^{O2} \times 10^4$	2.5030	0.0330	1.8903	1.3828	0.0135	0.9696
$t_0^{SO2} \times 10^4$	-0.7423	4.5087	-0.6244	-0.1517	1.8373	-0.1889
$t_0^{SO3} \times 10^4$	0.3395	3.0168	0.1936	0.3598	1.2294	0.1973
$z_0^{O2} \times 10^2$	23.838	0.356	22.928	10.687	0.313	10.406
$z_0^{SO2} \times 10^2$	2.977	4.776	2.787	1.246	3.912	2.370
$z_0^{SO3} \times 10^2$	0.523	2.712	0.395	0.700	1.742	0.606
$K \times 10^{-3}$, atm^{-1}	5.55	6.05	5.55	6.60	6.60	6.30
$-\Delta G/RT$	1.896	2.774	1.782	3.513	2.775	0.857
$\exp(-\Delta G/RT)$	6.673	16.010	5.940	33.63	16.045	2.357